Microreactor MRI

A team led by MSD Senior Faculty Scientist Alex Pines has adapted magnetic resonance imaging (MRI) for the study of gas-phase reactions on the microscale. This is a significant step towards improving the design of future catalysts and catalytic reactors and of microfluidic "lab-on-a-chip" devices.

Catalysis is vital to industrial chemistry, and the optimization of catalytic reactors attracts considerable R&D resources. Two long-standing but still unresolved challenges are to correlate the active regions in heterogeneous catalyst beds with their morphology and to monitor multistep reactions within the bed. Similar challenges exist in the evaluation of microfluidic chips which have chemistry components. MRI and nuclear magnetic resonance (NMR), its sister technology, are among the most powerful analytic tools known to science and, in principle, could be immensely valuable in these applications. However, until now, the low sensitivity of conventional MRI/NMR techniques has limited their usefulness in microscale research.

The key to the Berkeley group's success in enhancing sensitivity lay in their exploiting the properties of hydrogen gas (H_2). MRI/NMR signals arise from "spin," a property of almost all atomic nuclei. It gives rise to a magnetic moment: the nuclei act as if they were bar magnets with a north and south pole. Obtaining an MRI/NMR signal depends upon an excess of nuclei with spins pointing in one direction or the other – under normal conditions, this excess is very small, leading to weak signals. At standard temperature and pressure, hydrogen gas exists in one of two molecular forms – ortho (o-H_2) and para (p-H_2) – with the former making up about 75% of the mixture. In orthohydrogen, the spins of the two protons are pointed in the same direction, whereas in parahydrogen, the spins of the two protons point in opposite directions. In isolation, however, the spins of the large numbers of p-H_2 molecules cancel, so there is no net magnetic signal. However, if the p-H_2 participates in a hydrogenation reaction, the spins become inequivalent, and the resulting "hyperpolarization" can be passed on to the nuclei in the product molecules and used to boost the strength of their MRI/NMR signals by several orders of magnitude.

In this study, the researchers used a well-established method to prepare H_2 enriched in p-H_2 and reacted it with propylene gas to produce propane using Wilkinson's catalyst immobilized on a modified silica gel bed. The signal from the hyperpolarized propane was enhanced by a factor of 300 compared to the starting propylene and high-resolution 3-D maps of the catalytically active regions of the bed identified by the presence of the product propane, could be readily obtained. A more sophisticated polarization scheme allowed the flow patterns of the product to be visualized, as well. Thus, the new MRI/NMR technique provides the ability to directly measure the spatial dependence of chemical reaction and allows for direct comparisons to any simulations or assumptions used to design a catalytic reactor. The technique can be applied to other chemical reactions beyond hydrogenation, which significantly broadens its impact and potential use. It is also well-suited to the spatial dimensions of microfluidic reactors.

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Louis-S. Bouchard, Scott R. Burt, M. Sabieh Anwar, Kirill V. Kovtunov, Igor V. Koptyug, Alexander Pines, "NMR Imaging of Catalytic Hydrogenation in Microreactors with the Use of para-Hydrogen," *Science* **319**, 442 (2008).

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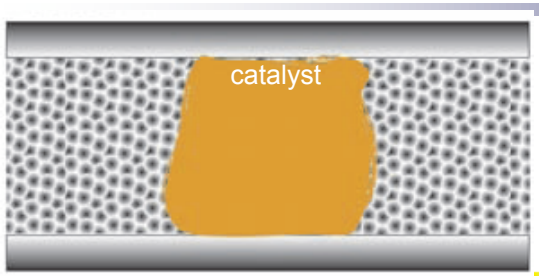
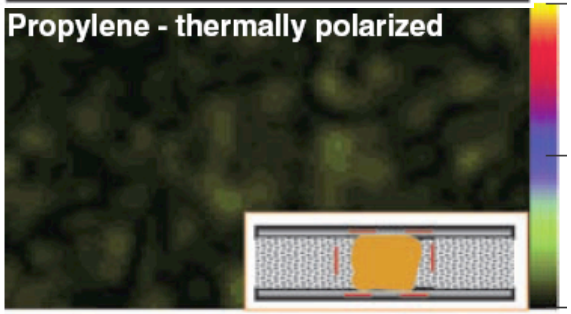
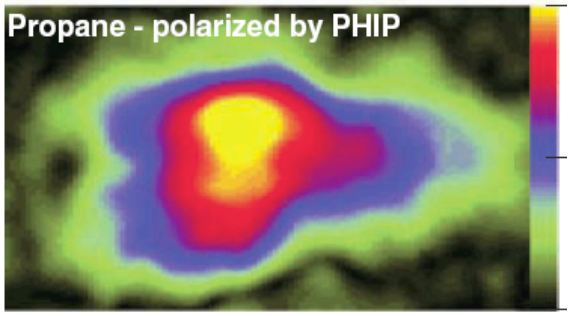
Microreactor MRI



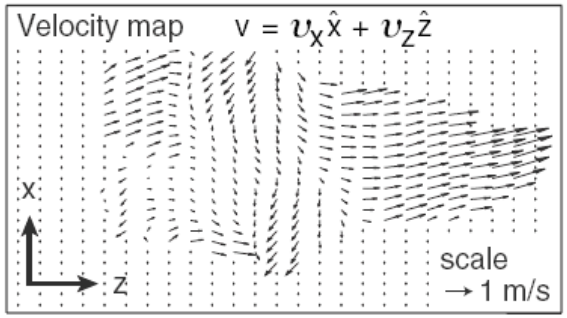
Schematic *of the reactor with the catalyst in the center region.*
propylene + H_2 -> propane



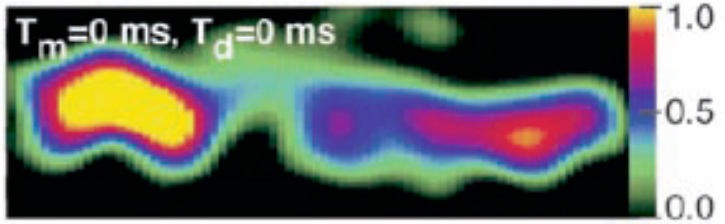
The MRI *signal from the thermally polarized reactant polypropylene is weak, as expected. The image is 2.3 mm x 7.0 mm*

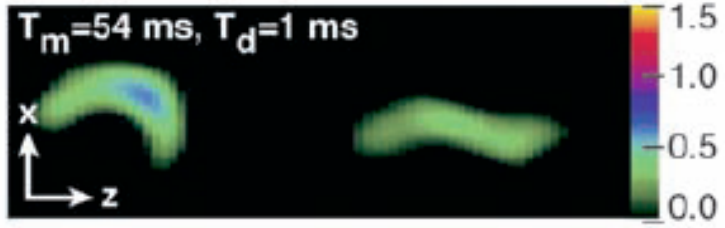


Reacting *propylene with para-H_2 produces "hyperpolarized" propane, which leads to a large increase in the MRI signal, easily allowing the active area of the catalyst bed to be visualized.*



Time resolved *measurements allows the velocity distribution of the produce molecules to be measured.*





Active areas *in a more heterogeneous bed (schematic above) can also be visualized as a function of reaction time.*